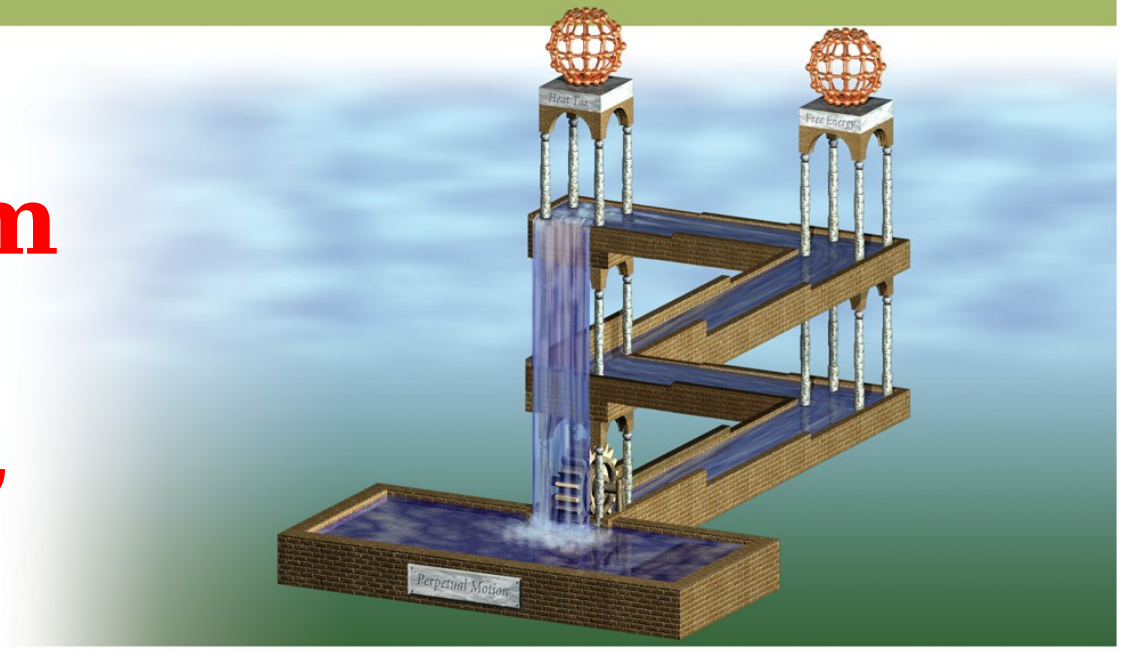
John E. McMurray – Robert C. Fay

GENERAL CHEMISTRY: ATOMS FIRST

Chapter 16 Thermodynamics: Entropy, Free Energy, and Equilibrium



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First Law of Thermodynamics Conservation of Energy

- **Energy cannot be Created or Destroyed**
  - ✓ the total energy of the universe cannot change
    - ➢ it can transfer it from one place to another

$$\Delta E_{universe} = 0 = \Delta E_{system} + \Delta E_{surroundings}$$

First Law of Thermodynamics

- for an exothermic reaction
  - ✓"lost" **system heat** goes into the **surroundings**
- energy is "lost" from a system,
  - **converted to heat, *q***
  - **used to do work, *w***
- energy conservation requires that:
  - $\Delta E_{system} = q + w$ (heat released + work done)
- ΔE is a *state function*
  - ✓independent of how you get there

Energy Tax

- every energy transition results in a "loss" of energy
  - ✓ conversion of energy to heat which is "lost" to the surroundin
- recharging a battery with 100 kJ of useful energy will require more than 100 kJ
- you can't win!
- you can't break even!

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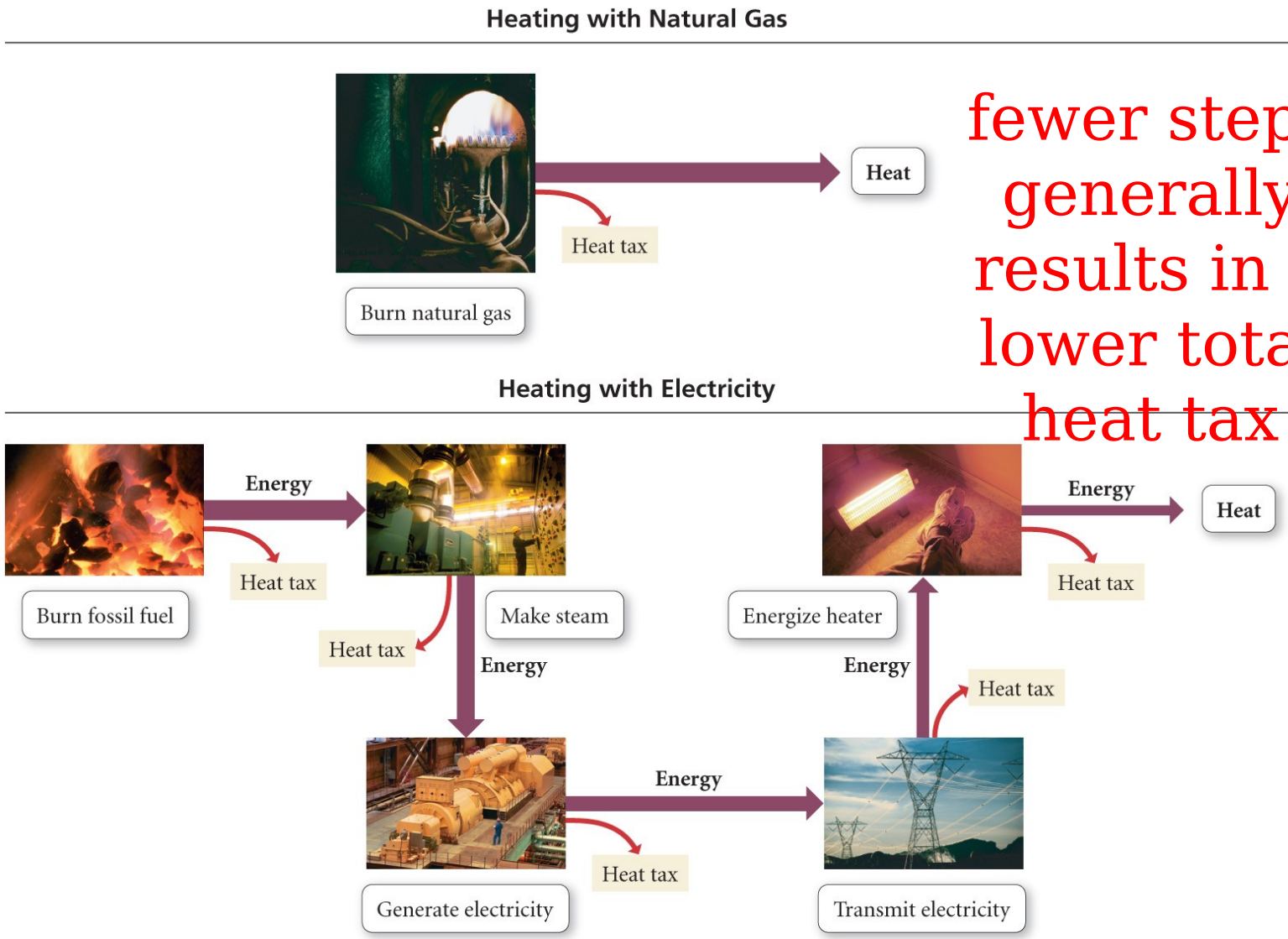
Heat Tax



fewer steps generally results in a lower total heat tax

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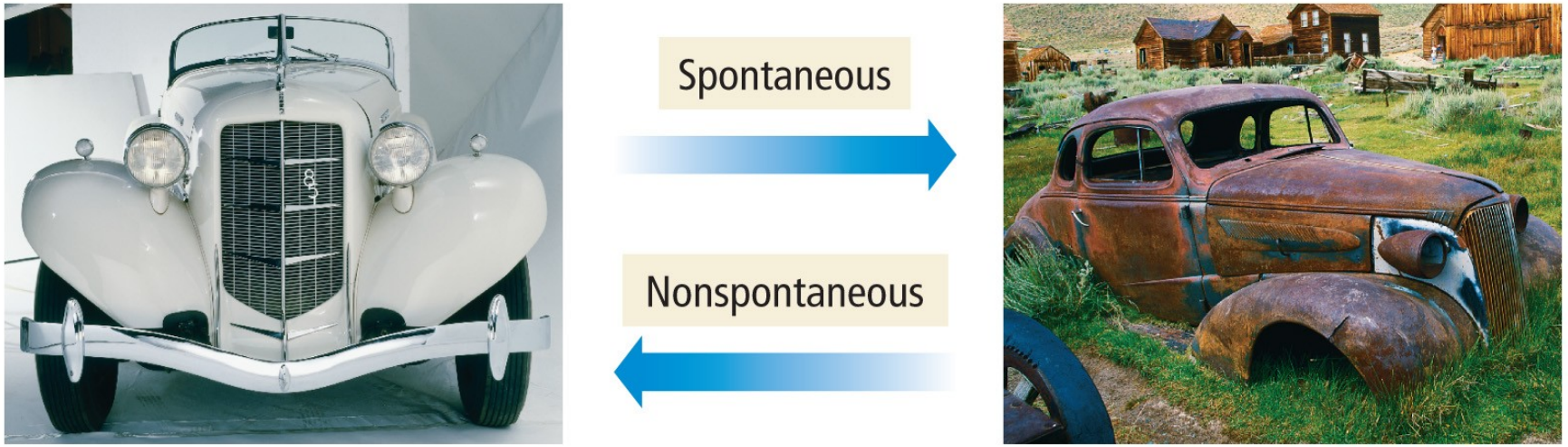
Thermodynamics and Spontaneity

- thermodynamics predicts whether a process will proceed under the given conditions
  - ✓ **spontaneous process**
  - ✓ **non-spontaneous process**
    - ➢ require energy input to go
- spontaneity is determined by comparing the **free energy** of the system before and after reaction.
  - ✓ if the system has less free energy after reaction than before the reaction, the reaction is thermodynamically favorable.

The direction of spontaneous process can be determined by comparing the potential energy of the system at the start and the end.

Reversibility of Process

- any spontaneous process is **irreversible**
- if a process is spontaneous in one direction, it must be non-spontaneous in the opposite direction
- a reversible process will result in no change in free energy



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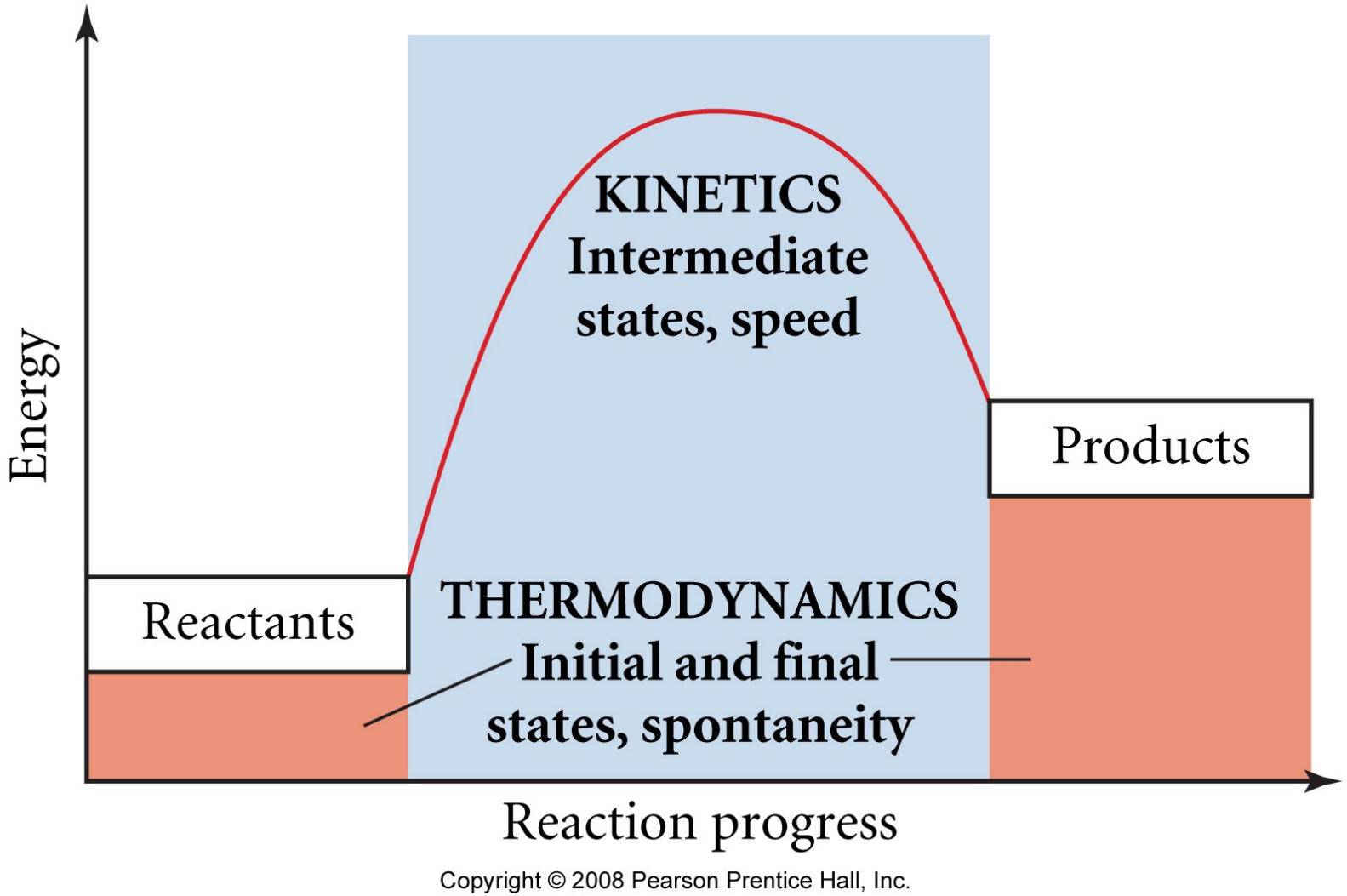
Thermodynamics vs. Kinetics



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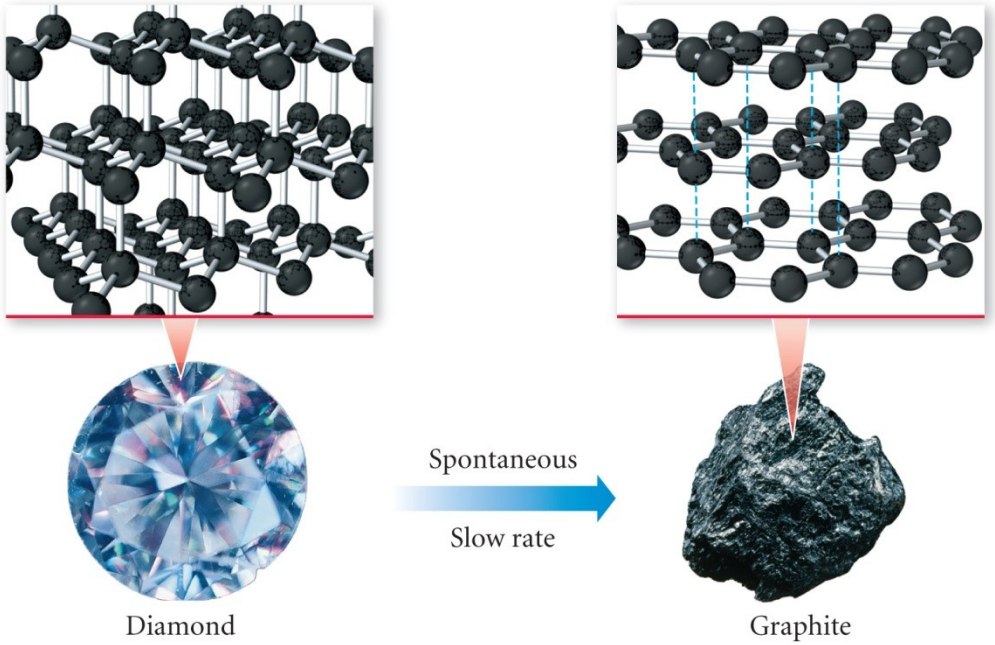
Diamond → Graphite



Graphite is more stable than diamond, so the conversion of diamond into graphite is spontaneous – but , it's so slow that your ring won't turn into pencil lead in your lifetime (or through many of your generations).

spontaneity ≠ fast or slow

Factors Affecting Rxn Spontaneity

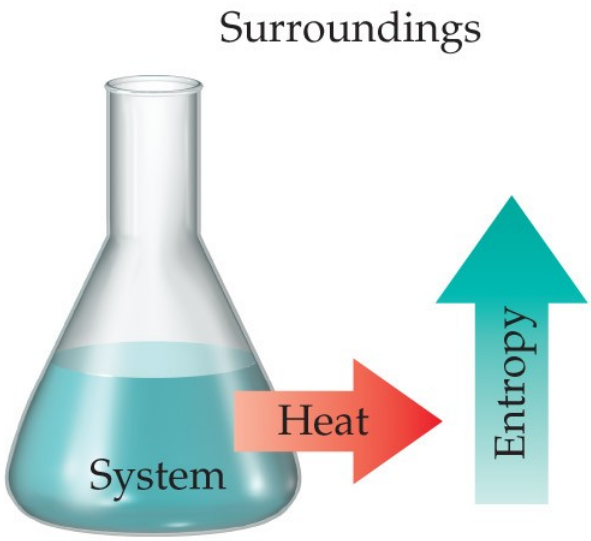
- **enthalpy** and **entropy**
  - ✓Determine thermodynamic favorability
  - ✓Enthalpy is generally more important than entropy

- **Enthalpy** compares the bond energy of reactants to products.
  - ✓ bond energy = amount needed to break a bond.
  - ✓ ΔH (enthalpy)
- **Entropy** relates to system randomness/orderliness
  - ✓ ΔS (entropy)

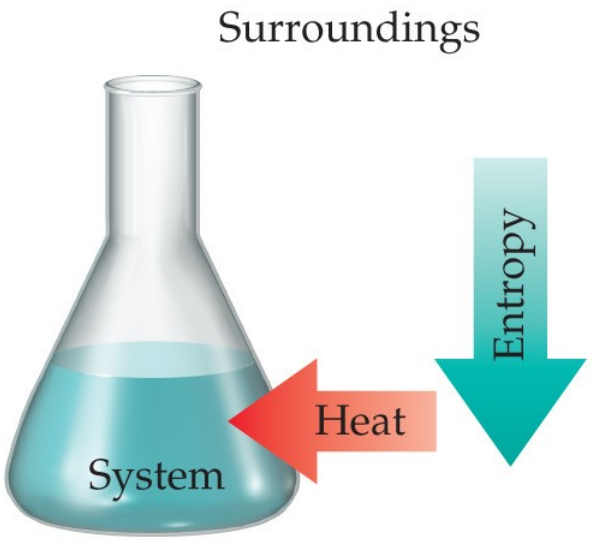
Enthalpy (ΔH in kJ/mol)

- related to the internal energy
- stronger bonds = more stable molecules
- if product stability > reactants, energy is released
  - ✓ **exothermic**
  - ✓ **ΔH = negative**
- if reactant stability > products, energy absorbed
  - ✓ **endothermic**
  - ✓ **ΔH = positive**
- Enthalpy is favorable for exothermic reactions and unfavorable for endothermic reactions.
- Hess' Law $\Delta H°_{rxn} = \Sigma(\Delta H°_{prod}) - \Sigma(\Delta H°_{react})$ [see ch:6]

Entropy and the Second Law of Thermodynamics



(a) When an exothermic reaction occurs in the system ($\Delta H < 0$), the surroundings gains heat and its entropy increases ($\Delta S_{surr} > 0$).



(b) When an endothermic reaction occurs in the system ($\Delta H > 0$), the surroundings loses heat and its entropy decreases ($\Delta S_{surr} < 0$).

Substance	ΔH° kJ/mol	Substance	ΔH° kJ/mol
Al(s)	0	Al_2O_3	-1669.8
$Br_2(l)$	0	$Br_2(g)$	+30.71
C(diamond)	+1.88	C(graphite)	0
CO(g)	-110.5	$CO_2(g)$	-393.5
Ca(s)	0	CaO(s)	-635.5
Cu(s)	0	CuO(s)	-156.1
Fe(s)	0	$Fe_2O_3(s)$	-822.16
$H_2(g)$	0	$H_2O_2(l)$	-187.8
$H_2O(g)$	-241.82	$H_2O(l)$	-285.83
HF(g)	-268.61	HCl(g)	-92.30
HBr(g)	-36.23	HI(g)	+25.94
$I_2(s)$	0	$I_2(g)$	+62.25
$N_2(g)$	0	$NH_3(g)$	-46.19
NO(g)	+90.37	$NO_2(g)$	+33.84
Na(s)	0	$O_2(g)$	0
S(s)	0	$SO_2(g)$	-296.9

Entropy (S in J/mol)

- **entropy** is a thermodynamic function that increases as the number of energetically equivalent ways of arranging the components increases
- $S = k \ln W$

  ✓ k = Boltzmann Constant = 1.38×10^{-23} J/K
  - the gas constant "R" divided by Avogadro's number =
  - 8.314 J/mol-K ÷ 6.02×10^{23}

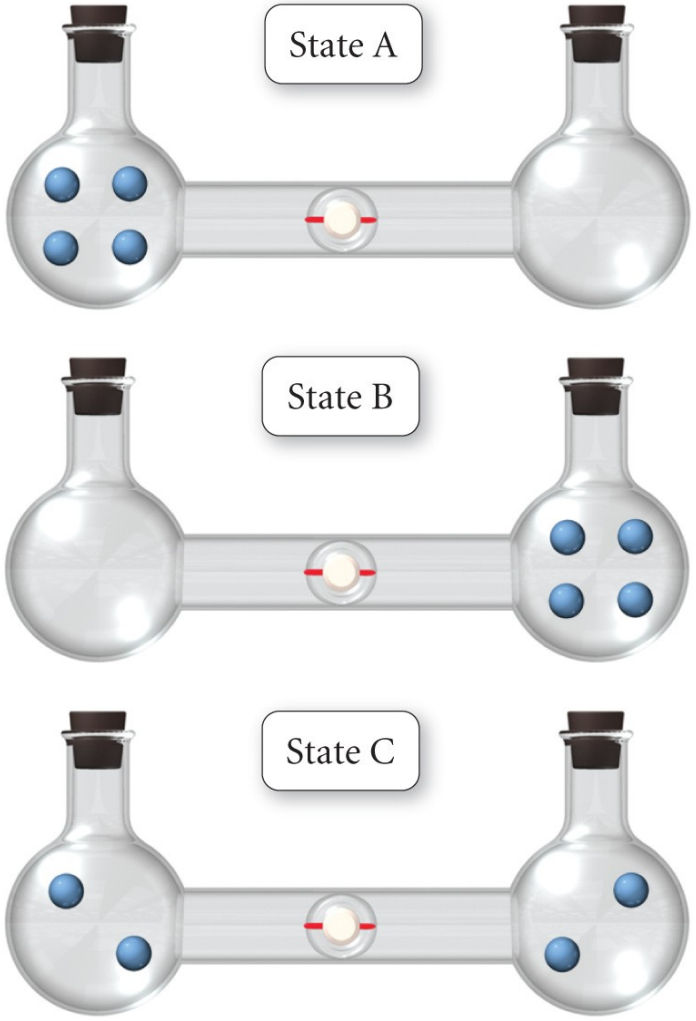
  ✓ W is the number of energetically equivalent states (unitless)

- Random systems require less energy than ordered systems

W

Energetically Equivalent States for the Expansion of a Gas

We have omitted the states with 1 and 3 particles for simplification.



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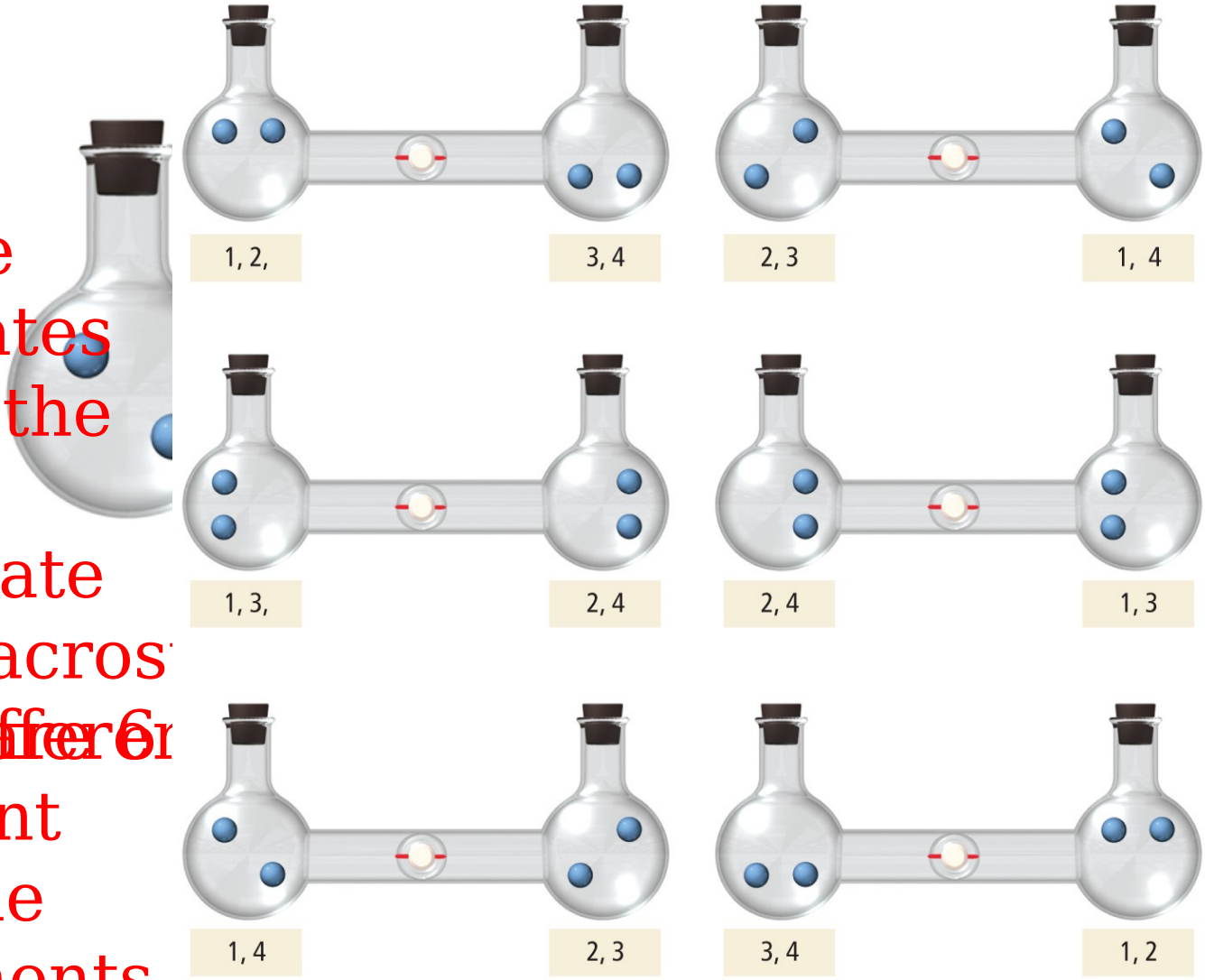
Macrostates → Microstates



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These microstates all have the same macrostate

This macros

Several differe

So there are 6 different particle arrangements that result in the same

es

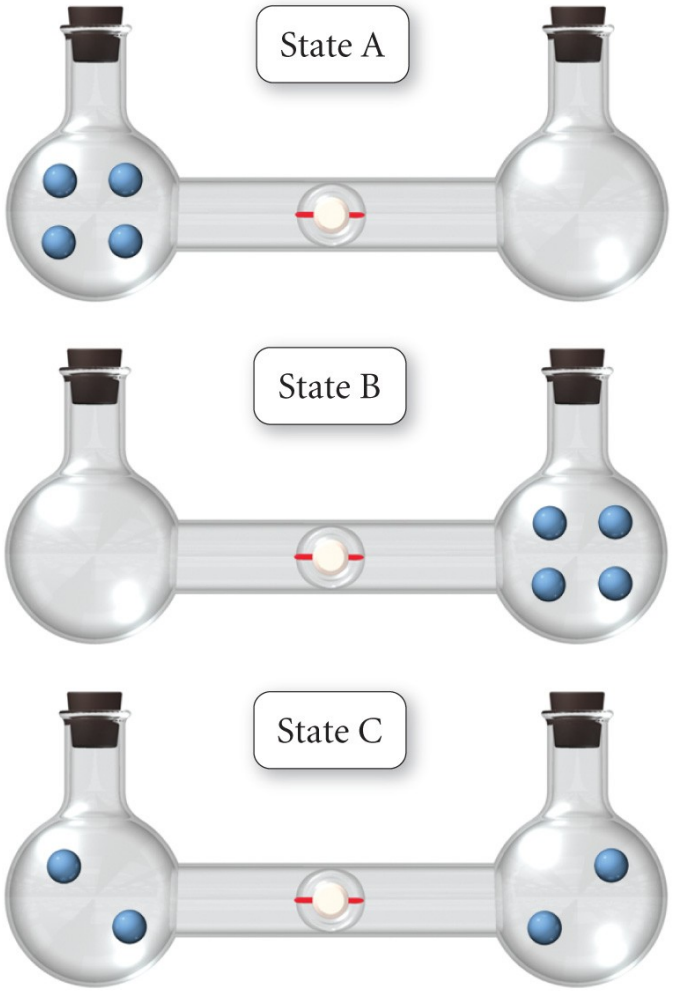
Macrostates and Probability

There is only one possible arrangement that gives State A and one that gives State B

There are 6 possible arrangements that give State C

Therefore State C has higher entropy than either State A or State B

The macrostate with the highest entropy also has the greatest dispersal of energy



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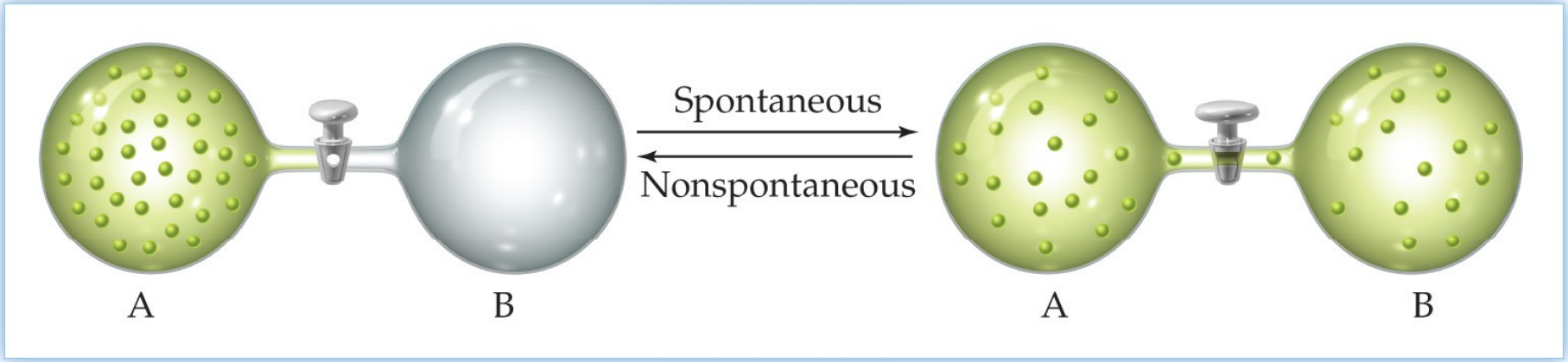
Spontaneous Processes

Spontaneous Process: A process that, once started, proceeds on its own without a continuous external influence.



Changes in Entropy, ΔS

- entropy change is **favorable** when the result is a more random system.
  - ✓ **ΔS is positive**
- Changes that increase entropy are:
  - ✓ reactions where products are in a more disordered state. (solid => liquid => gas)
  - ✓ reactions which have a larger number of product molecules than reactant molecules.
  - ✓ **increase in temperature**
  - ✓ solids dissociating into ions upon dissolving

Entropy and the Second Law of Thermodynamics

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

or

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

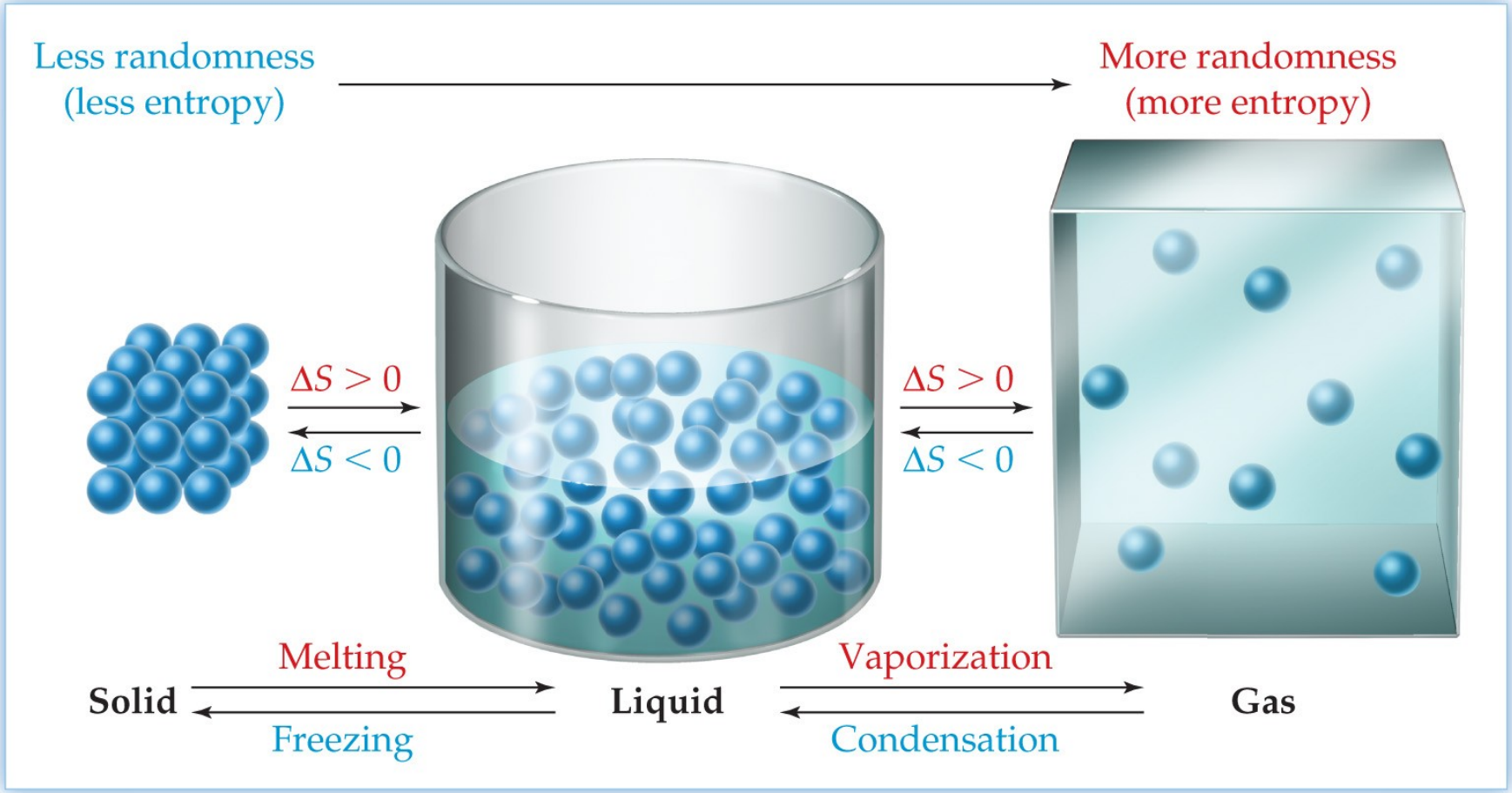
$\Delta S_{\text{total}} > 0$ The reaction is spontaneous.

$\Delta S_{\text{total}} < 0$ The reaction is nonspontaneous.

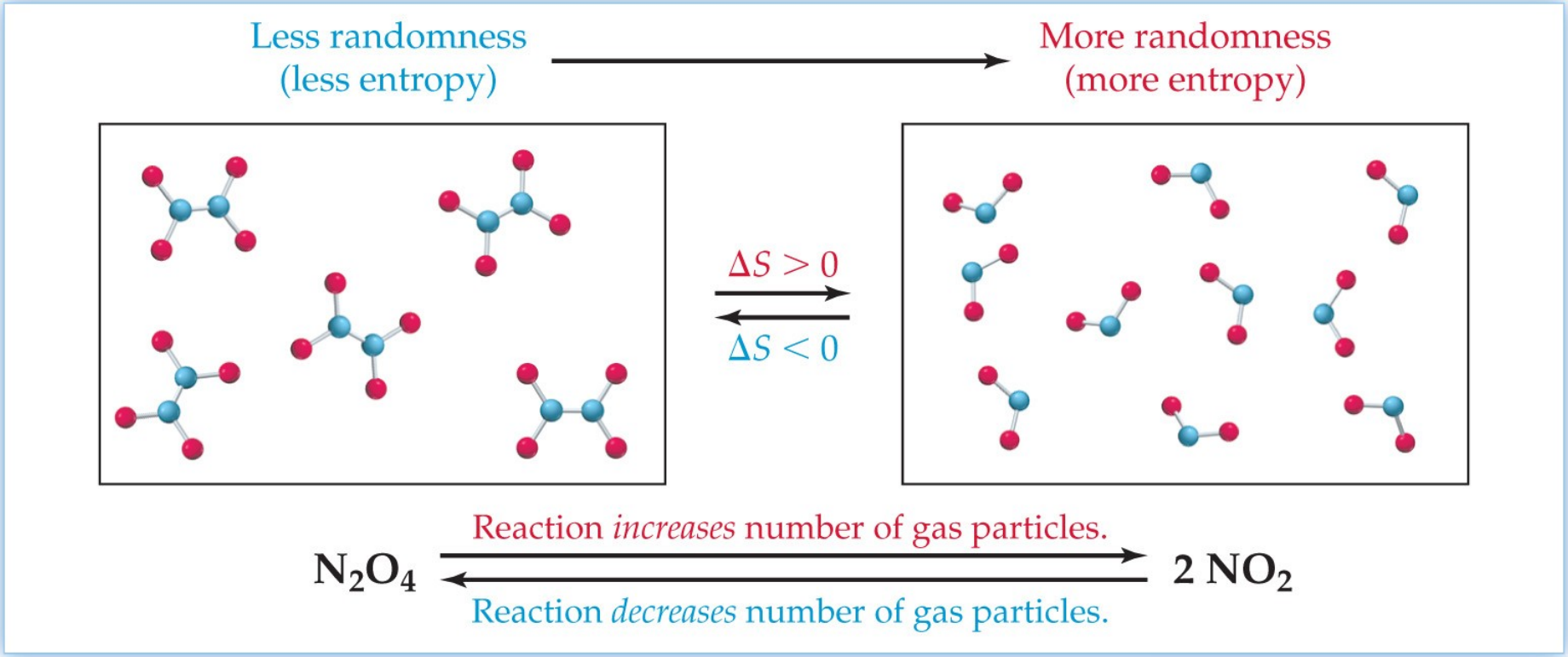
$\Delta S_{\text{total}} = 0$ The reaction mixture is at equilibrium.

Enthalpy, Entropy, and Spontaneous Processes

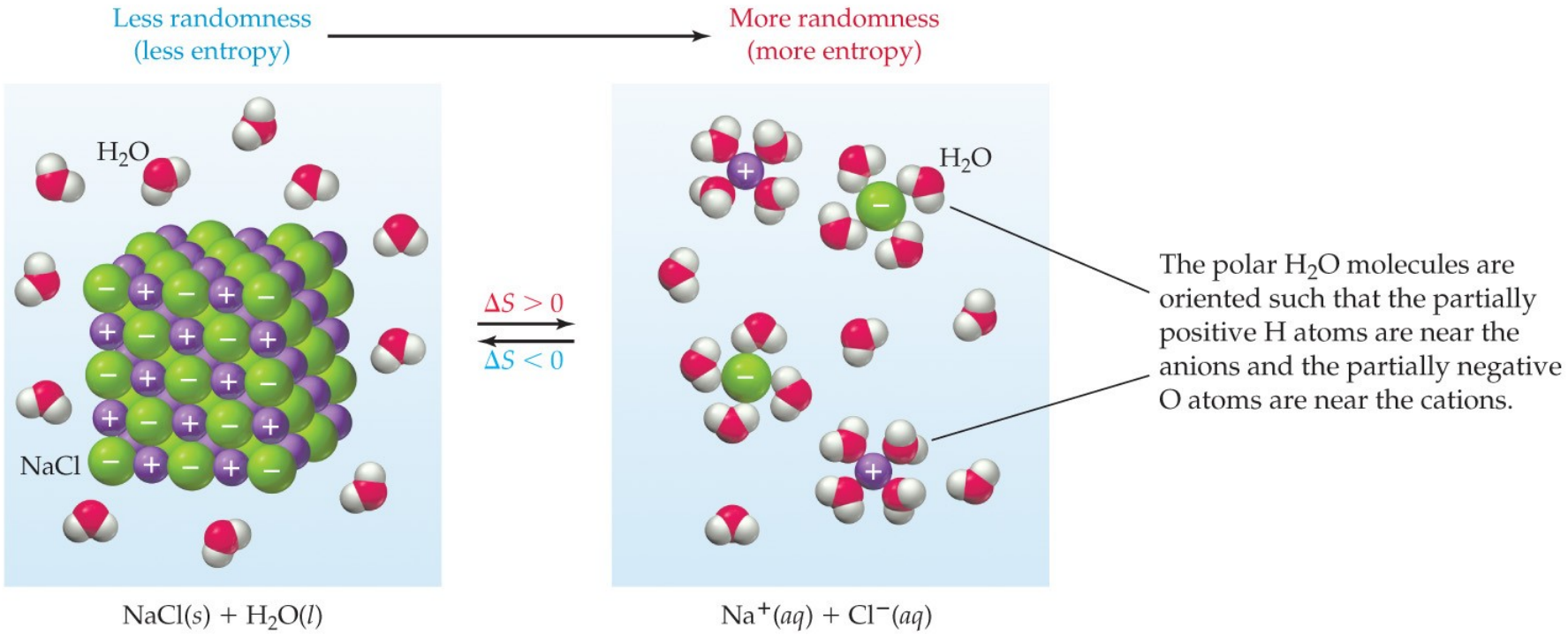
$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$



Enthalpy, Entropy, and Spontaneous Processes



Enthalpy, Entropy, and Spontaneous Processes


Less randomness
(less entropy)
More randomness
(more entropy)
H_2O
NaCl
$\Delta S > 0$
$\Delta S < 0$
H_2O
The polar H_2O molecules are oriented such that the partially positive H atoms are near the anions and the partially negative O atoms are near the cations.
$NaCl(s) + H_2O(l)$
$Na^+(aq) + Cl^-(aq)$

Disruption of the crystal increases the entropy, but the hydration process decreases the entropy. For the dissolution of NaCl, the net effect is an entropy increase.

The 2nd Law of Thermodynamics

- **the total entropy change of the universe must be positive ($\Delta S_{\text{universe}} > 0$) for a process to be spontaneous and irreversible**
  - ✓ for reversible process $\Delta S_{\text{univ}} = 0$

$$\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

- If entropy of the system decreases, then entropy of the surroundings must increase by a larger amount
  - ✓ when ΔS_{system} is negative, $\Delta S_{\text{surroundings}}$ is positive
- the increase in $\Delta S_{\text{surroundings}}$ often comes from the heat released in an exothermic reaction

Entropy Change in State Change

- when materials change state, the number of macrostates it can have changes as well
  - ✓for entropy: solid < liquid < gas
  - ✓because the degrees of freedom of motion increases solid → liquid → gas

Heat Flow, Entropy, and the 2nd Law

Heat must flow from water to ice in order for the entropy of the universe to increase

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Temperature Dependence of Entropy $\Delta S_{surroundings}$

- when a process is exothermic, it adds heat to the surroundings, increasing the entropy of the surroundings
- when a system process is endothermic, it takes heat from the surroundings, decreasing the entropy of the surroundings
- the amount $S_{surroundings}$ (entropy) changes, depends on the starting temperature
  - ✓ the higher the starting temperature, the less effect addition or removal of heat has

Gibbs Free Energy “G”

$$\Delta S_{surroundings} = \frac{-\Delta H_{system}}{T}$$

Entropy = Enthalpy / temperature

$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings}$$

$$\Delta S_{univ} = \Delta S_{sys} - \Delta H_{sys} / T$$

Combine 1st and 2nd equations

Multiply by (– T)

$$-T\Delta S_{univ} = -T\Delta S_{sys} + \Delta H_{sys}$$

Rearrange equation

$$-T\Delta S_{univ} = \Delta H_{sys} - T\Delta S_{sys}$$

Define ΔG (Gibbs free energy)

$$\Delta G_{sys} = -T\Delta S_{universe}$$

$$\Delta G_{reaction} = \Sigma n\Delta G_{products} - \Sigma$$

Combine last 2 equations

Gibbs Free Energy, ΔG

- Is the max amt of energy from the system available to do work on the surroundings
- when **$\Delta G < 0$**, the **process will be spontaneous**
  - ✓ **ΔG is negative means energy** is released into the surroundings
- **$\Delta G > 0$, non-spontaneous**

Gibbs Free Energy, ΔG

ΔG < 0 when	**ΔH < 0**	**ΔS > 0**	**Exothermic & more random**
Or when	ΔH < 0 and large	ΔS < 0 but small	
Or when	ΔH > 0 and small	ΔS > 0 and large	Or at high temperature

ΔG > 0 when	**ΔH > 0**	**ΔS < 0**	**Never spontaneous at any temperature**

- when $\Delta G = 0$ the reaction is at **equilibrium**

Free Energy

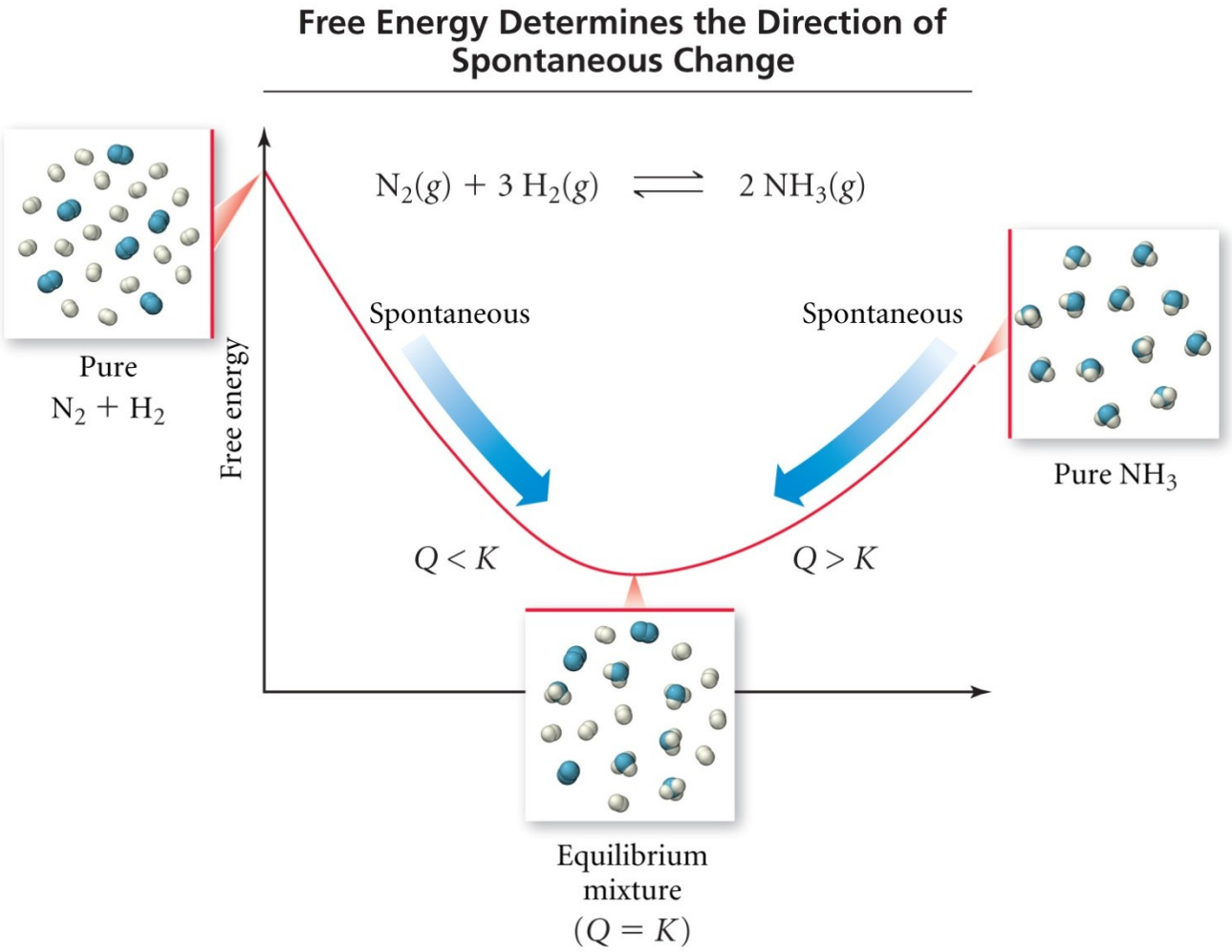
Using the second law and $\Delta G = \Delta H - T\Delta S = -T\Delta S_{\text{total}}$

$\boldsymbol{\Delta G < 0}$	The reaction is spontaneous.
$\boldsymbol{\Delta G > 0}$	The reaction is nonspontaneous.
$\boldsymbol{\Delta G = 0}$	The reaction mixture is at equilibrium.

The reaction $C_3H_{8(g)} + 5\ O_{2(g)} \rightarrow 3\ CO_{2(g)} + 4\ H_2O_{(g)}$ has $\Delta H_{rxn} = -2044$ kJ at 25°C. Calculate the entropy change of the surroundings.

Given:	$\Delta H_{system} = -2044$ kJ, T = 298 K
Find:	$\Delta S_{surroundings}$, J/K
Concept Plan:	T, ΔH ⇒ ΔS $\Delta S_{surr} = \frac{-\Delta H_{sys}}{T}$
Relationships/ Solutions:	$\Delta S_{surr} = \frac{-\Delta H_{sys}}{T} = \frac{-(-2044\ kJ)}{298\ K}$ $\Delta S_{surr} = 6.86 \frac{kJ}{K} = 6.86 \times 10^3 \frac{J}{K}$
Check:	combustion is largely exothermic, so the entropy of the surrounding should increase significantly

Free Energy Change and Spontaneity



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ΔG, ΔH, and ΔS

TABLE 17.1 The Effect of ΔH, ΔS, and T on Spontaneity

ΔH	ΔS	Low Temperature	High Temperature	Example
−	+	Spontaneous ($\Delta G < 0$)	Spontaneous ($\Delta G < 0$)	$2\,N_2O(g) \longrightarrow 2\,N_2(g) + O_2(g)$
+	−	Nonspontaneous ($\Delta G > 0$)	Nonspontaneous ($\Delta G > 0$)	$3\,O_2(g) \longrightarrow 2\,O_3(g)$
−	−	Spontaneous ($\Delta G < 0$)	Nonspontaneous ($\Delta G > 0$)	$H_2O(l) \longrightarrow H_2O(s)$
+	+	Nonspontaneous ($\Delta G > 0$)	Spontaneous ($\Delta G < 0$)	$H_2O(l) \longrightarrow H_2O(g)$

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The reaction $CCl_{4(g)} \rightarrow C_{(s,\ graphite)} + 2\ Cl_{2(g)}$ has $\Delta H = +95.7$ kJ and $\Delta S = +142.2$ J/K at 25°C. Calculate ΔG and determine if it is spontaneous.

Given:	$\Delta H = +95.7$ kJ, $\Delta S = 142.2$ J/K, T = 298 K
Find:	ΔG, kJ
Concept Plan:	T, ΔH, ΔS ⟹ ΔG $\Delta G = \Delta H - T\Delta S$
Relationships/ Solutions:	$\Delta G = \Delta H - T\Delta S$ $= \left(+95.7 \times 10^3\ \text{J}\right) - \left(298\ \text{K}\right)\left(+142.2\ \frac{\text{J}}{\text{K}}\right)$ $= +5.33 \times 10^4\ \text{J}$
Answer:	Since ΔG is +, the reaction is not spontaneous at this temperature. To make it spontaneous, we need to increase the temperature

The reaction $CCl_{4(g)} \rightarrow C_{(s,\ graphite)} + 2\ Cl_{2(g)}$ has $\Delta H = +95.7$ kJ and $\Delta S = +142.2$ J/K. Calculate the minimum temperature it will be spontaneous.

Given:	$\Delta H = +95.7$ kJ, $\Delta S = 142.2$ J/K, $\Delta G < 0$ to be spontaneous
Find:	T, K
Concept Plan:	$\Delta G, \Delta H, \Delta S \Rightarrow T$ $\Delta G = \Delta H - T\Delta S$
Relationships:	$\Delta G = (\Delta H - T\Delta S) < 0$
Solution:	$(+95.7 \times 10^3\ \text{J}) - (T)\left(+142.2 \frac{\text{J}}{\text{K}}\right) < 0$ $(+95.7 \times 10^3\ \text{J}) < (T)\left(+142.2 \frac{\text{J}}{\text{K}}\right)$ $\frac{(+95.7 \times 10^3\ \text{J})}{\left(+142.2 \frac{\text{J}}{\text{K}}\right)} < T$ $673\ \text{K} < T$
Answer:	The temperature must be higher than 673K for the reaction to be spontaneous

Standard States

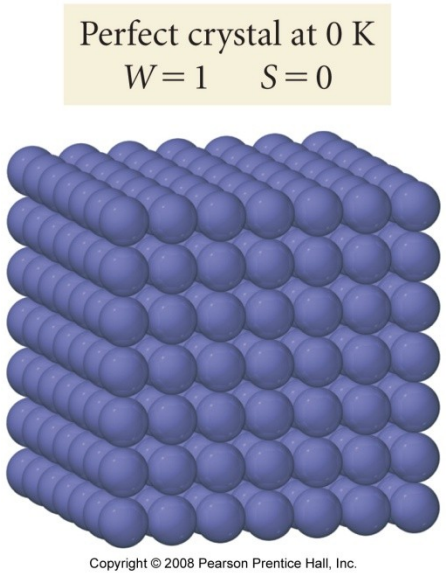
- For a pure gas:
  - ✓ P = 1 atm.
- For a liquid or solid:
  - ✓ Pure substance in its most stable form
  - ✓ 1 atm. and 25˚C
- For a solution:
  - ✓ A concentration of exactly 1M

Standard Entropies, S°

- ΔS° is the standard entropy (S°) for a process where all reactants and products are in their std states.
  - ✓ entropies for 1 mole at 298 K for a particular state, a particular allotrope, particular molecular complexity, a particular molar mass, and a particular degree of dissolution
  - ✓ units of J/mol-K mean that S° is an extensive property, i.e. based on the amount of the substance

The 3rd Law of Thermodynamics Absolute Entropy

- **absolute entropy** is the amount of energy it has due to dispersion of energy through its particles
- 3rd Law states, for a perfect crystal at absolute zero, the absolute entropy = 0 J/mol•K
  - ✓ Since S = k(lnW), a perfect crystal will have W=1 and thus lnW=0, therefore S=0
  - ✓ every substance that is not a perfect crystal at absolute zero has some energy from entropy
  - ✓ therefore, the absolute entropy of substances is always +



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Substance	S° J/mol-K	Substance	S° J/mol-K
Al(s)	28.3	$Al_2O_3(s)$	51.00
$Br_2(l)$	152.3	$Br_2(g)$	245.3
C(diamond)	2.43	C(graphite)	5.69
CO(g)	197.9	$CO_2(g)$	213.6
Ca(s)	41.4	CaO(s)	39.75
Cu(s)	33.30	CuO(s)	42.59
Fe(s)	27.15	$Fe_2O_3(s)$	89.96
$H_2(g)$	130.58	$H_2O_2(l)$	109.6
$H_2O(g)$	188.83	$H_2O(l)$	69.91
HF(g)	173.51	HCl(g)	186.69
HBr(g)	198.49	HI(g)	206.3
$I_2(s)$	116.73	$I_2(g)$	260.57
$N_2(g)$	191.50	$NH_3(g)$	192.5
NO(g)	210.62	$NO_2(g)$	240.45
Na(s)	51.45	$O_2(g)$	205.0
S(s)	31.88	$SO_2(g)$	248.5

Relative Standard Entropies States

- the gas state has a larger entropy than the liquid state at a particular temperature
- the liquid state has a larger entropy than the solid state at a particular temperature

Substance	S°, (J/mol•K)
H_2O (*s*)	70.0
H_2O (*l*)	188.8

Relative Standard Entropies Molar Mass

- the larger the molar mass, the larger the entropy
- available energy states more closely spaced, allowing more dispersal of energy through the states

	$S°$ (J/mol·K)	
He(g)	126.2	
Ne(g)	146.1	
Ar(g)	154.8	
Kr(g)	163.8	
Xe(g)	169.4	

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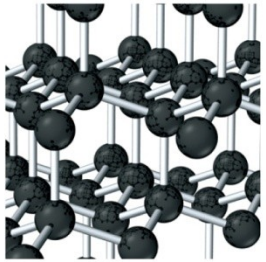
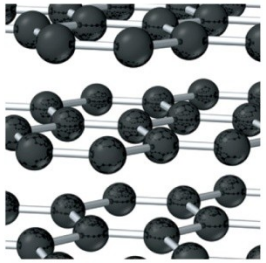
Relative Standard Entropies Allotropes

- the less constrained the structure of an allotrope is, the larger its entropy
- Diamond = 3d while graphite is 2d

	$S°$ (J/mol·K)	
C(*s*, diamond)	2.4	
C(*s*, graphite)	5.7	

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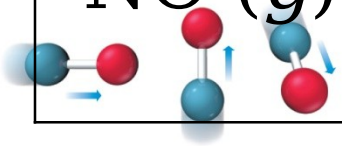
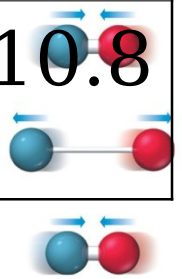
Relative Standard Entropies Molecular Complexity

- larger, more complex molecules generally have larger entropy
- more available energy states, allowing more dispersal of energy through the states

Substance	Molar Mass	S°, (J/mol•K)
Ar (*g*)	39.948	154.8
NO (*g*)	30.006	210.8





Translational motion Rotational motion Vibrational motion

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Relative Standard Entropies Dissolution

- dissolved solids generally have larger entropy than the solids themselves
- distributing solute particles throughout the solvent

Substance	S°, (J/mol•K)
$KClO_3(s)$	143.1
$KClO_3(aq)$	265.7

Calculate ΔS° for the reaction

$4\ NH_{3(g)} + 5\ O_{2(g)} \rightarrow 4\ NO_{(g)} + 6\ H_2O_{(g)}$

Substance	S°, J/mol·K
$NH_3(g)$	192.8
$O_2(g)$	205.2
$NO(g)$	210.8
$H_2O(g)$	188.8

Given:	standard entropies from Appendix IIB
Find:	ΔS, J/K
Concept Plan:	S°_{NH3}, S°_{O2}, S°_{NO}, S°_{H2O}, → ΔS $\Delta S^\circ = \left(\Sigma n_p S^\circ_{products}\right) - \left(\Sigma n_r S^\circ_{reactants}\right)$
Relationships:	$\Delta S^\circ = \left(\Sigma n_p S^\circ_{products}\right) - \left(\Sigma n_r S^\circ_{reactants}\right)$
Solution:	$= [4(S^\circ_{NO(g)}) + 6(S^\circ_{H_2O(g)})] - [4(S^\circ_{NH_3(g)}) + 5(S^\circ_{O_2(g)})]$ $= [4(210.8\ \frac{J}{K}) + 6(188.8\ \frac{J}{K})] - [4(192.8\ \frac{J}{K}) + 5(205.2\ \frac{J}{K})]$ $= 178.8\ \frac{J}{K}$
Check:	ΔS is +, as you would expect for a reaction with more gas product molecules than reactant molecules

Calculating ΔG°

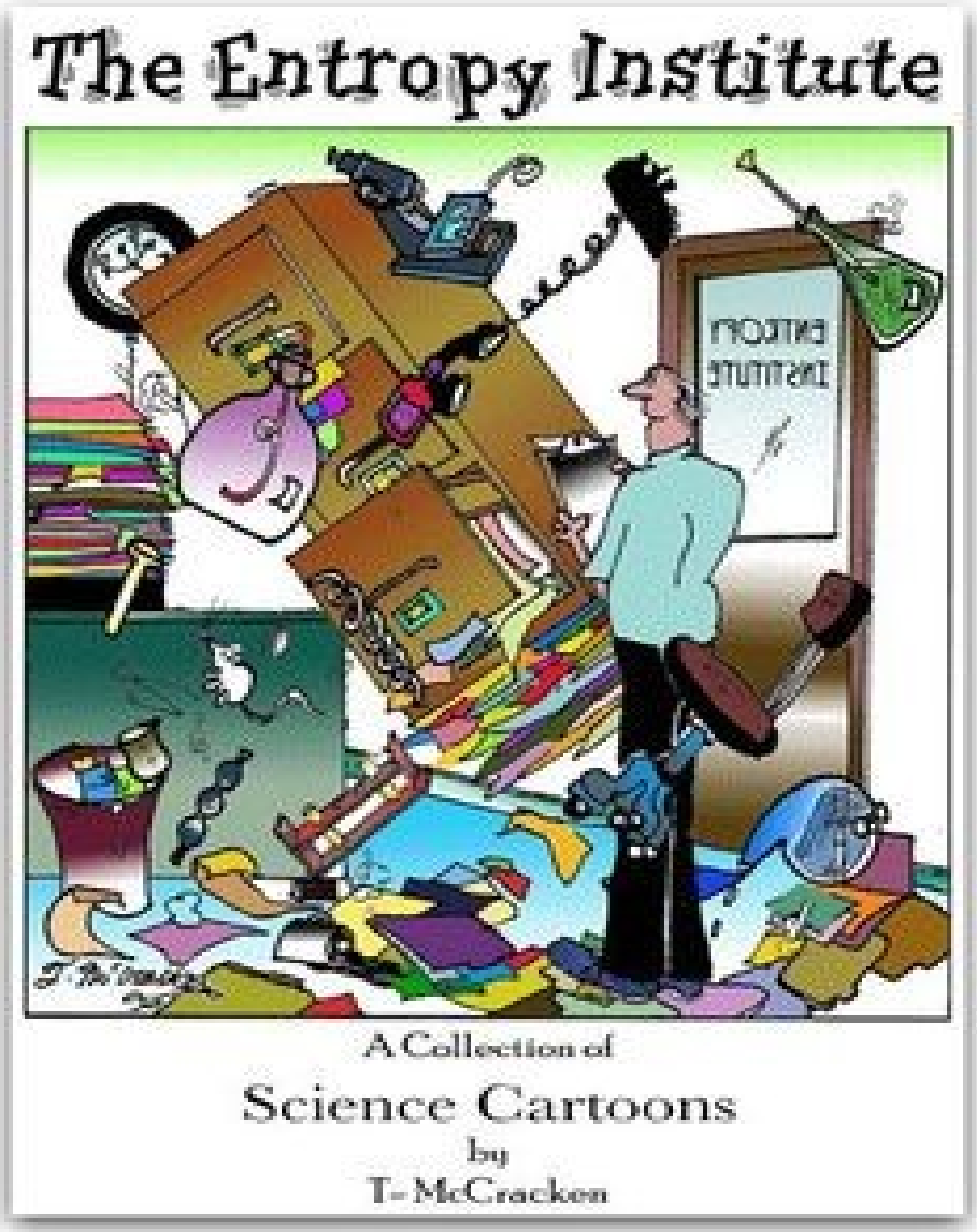
- at 25°C:

$$\Delta G^\circ_{reaction} = \Sigma n G^\circ_f(products) - \Sigma n G^\circ_f(reactants)$$

- at temperatures other than 25°C:
  - ✓ assuming the change in $\Delta H^\circ_{reaction}$ and $\Delta S^\circ_{reaction}$ is negligible

$$\boldsymbol{\Delta G^\circ_{reaction} = \Delta H^\circ_{reaction} - T\Delta S^\circ_{reaction}}$$

Substance	ΔG°_f kJ/mol	Substance	ΔG°_f kJ/mol
Al(s)	0	Al_2O_3	-1576.5
$Br_2(l)$	0	$Br_2(g)$	+3.14
C(diamond)	+2.84	C(graphite)	0
CO(g)	-137.2	$CO_2(g)$	-394.4
Ca(s)	0	CaO(s)	-604.17
Cu(s)	0	CuO(s)	-128.3
Fe(s)	0	$Fe_2O_3(s)$	-740.98
$H_2(g)$	0	$H_2O_2(l)$	-120.4
$H_2O(g)$	-228.57	$H_2O(l)$	-237.13
HF(g)	-270.70	HCl(g)	-95.27
HBr(g)	-53.22	HI(g)	+1.30
$I_2(s)$	0	$I_2(g)$	+19.37
$N_2(g)$	0	$NH_3(g)$	-16.66
NO(g)	+86.71	$NO_2(g)$	+51.84
Na(s)	0	$O_2(g)$	0
S(s)	0	$SO_2(g)$	-300.4



Three Laws of Thermodynamics (paraphrased):

First Law: You can't get anything without working for it.

Second Law: The most you can accomplish by work is to break even.

Third Law: You can't break even.

Calculate ΔG° at 25°C for the reaction

$CH_{4(g)} + 8\ O_{2(g)} \rightarrow CO_{2(g)} + 2\ H_2O_{(g)} + 4\ O_{3(g)}$

Substance	ΔG°_f, kJ/mol
$CH_4(g)$	-50.5
$O_2(g)$	0.0
$CO_2(g)$	-394.4
$H_2O(g)$	-228.6
$O_3(g)$	163.2

Given: standard free energies of formation from Appendix IIB

Find: ΔG°, kJ

Concept Plan: ΔG°_f of prod & react → ΔG°

$$\Delta G^\circ = \left(\Sigma n_p \Delta G^\circ_{f\,\text{products}}\right) - \left(\Sigma n_r \Delta G^\circ_{f\,\text{reactants}}\right)$$

Relationships:

Solution:

$$\Delta G^\circ = \left(\Sigma n_p \Delta G^\circ_{f\,\text{products}}\right) - \left(\Sigma n_r \Delta G^\circ_{f\,\text{reactants}}\right)$$

$$= [(\Delta G^\circ_{f\,CO_2}) + 2(\Delta G^\circ_{f\,H_2O}) + 4(\Delta G^\circ_{f\,O_3})] - [(\Delta G^\circ_{f\,CH_4}) + 8(\Delta G^\circ_{f\,O_2})]$$

$$= [(-394.4\ \text{kJ}) + 2(-228.6\ \text{kJ}) + 4(+163.2\ \text{kJ})] - [(-50.5\ \text{kJ}) + 8(0.0\ \text{kJ})]$$

$$= -1483\ \text{kJ}$$

ΔG is negative, process is spontaneous

The reaction $SO_{2(g)} + ½\ O_{2(g)} \rightarrow SO_{3(g)}$ has ΔH° = -98.9 kJ and ΔS° = -94.0 J/K at 25°C. Calculate ΔG° at 125°C and determine if it is spontaneous.

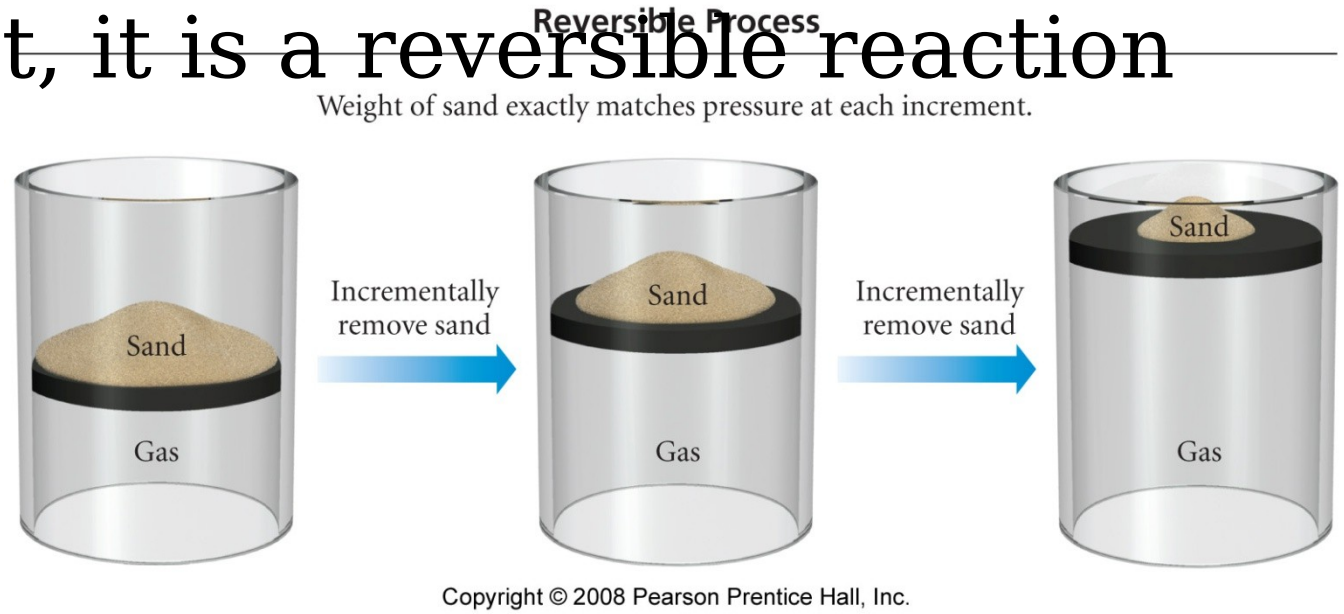
Given:	ΔH° = -98.9 kJ, ΔS° = -94.0 J/K, T = 398 K
Find:	ΔG°, kJ
Concept Plan:	T, ΔH°, ΔS° ⟹ ΔG° $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Relationships:	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
Solution:	$= (-98.9 \times 10^3\ J) - (398\ K)\left(-94.0 \frac{J}{K}\right)$ $= -61.5 \times 10^3\ J = -61.5\ kJ$
Answer:	Since ΔG is -, the reaction is spontaneous at this temperature, though less so than at 25°C

ΔG Relationships

- if a reaction can be expressed as a series of reactions, the sum of the ΔG values of the individual reaction is the ΔG of the total reaction
  - ✓ ΔG is a state function
- if a reaction is reversed, the sign of its ΔG value reverses
- if the amounts of materials is multiplied by a factor, the value of the ΔG is multiplied by the same factor
  - ✓ the value of ΔG of a reaction is extensive, i.e. depends on the amount of material

Free Energy and Reversible Reactions

- the change in free energy is a theoretical limit for the amount of work that can be done
- if the reaction achieves its theoretical limit, it is a reversible reaction



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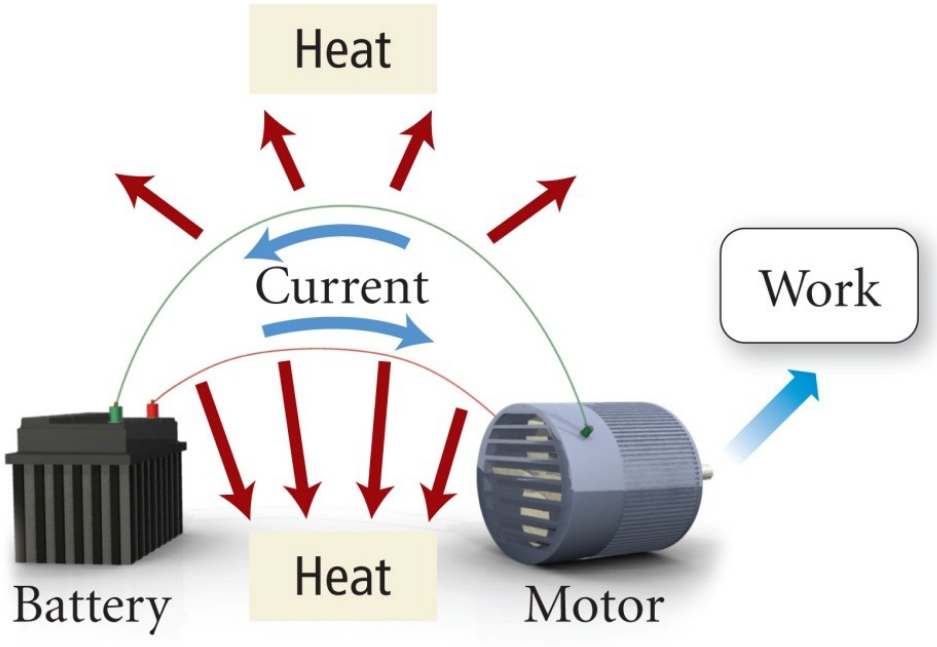
Real Reactions

- in a real reaction, some, if not most of the free energy is “lost” as heat
- therefore, real reactions are irreversi



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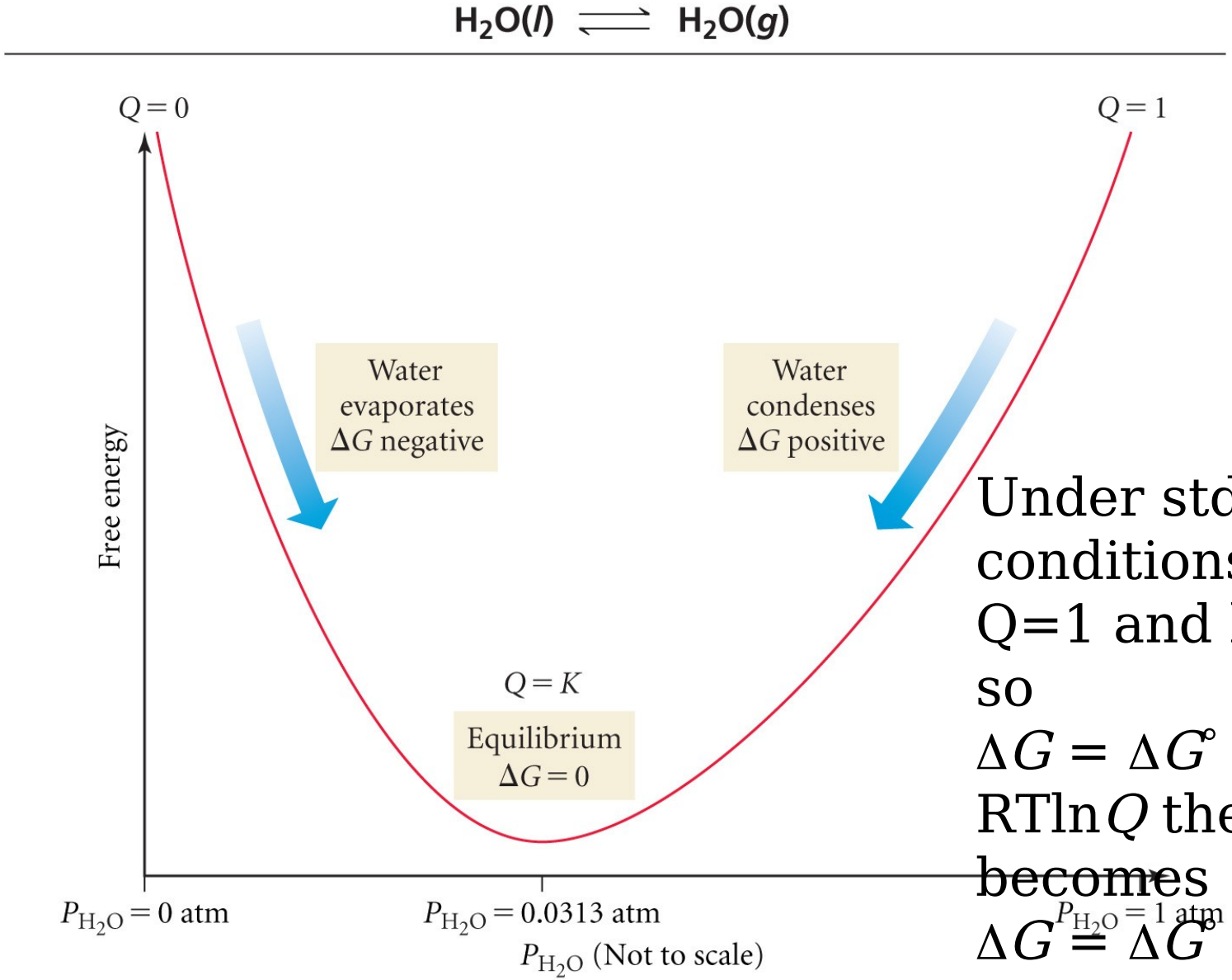
ΔG under Nonstandard Conditions

- $\Delta G = \Delta G^\circ$ only when the reactants and products are in their standard states
  - their normal state at that temperature
  - partial pressure of gas = 1 atm
  - concentration = 1 M
- under nonstandard conditions, $\Delta G = \Delta G^\circ + \mathrm{RTln}Q$
  - Q is the reaction quotient
- at equilibrium $\Delta G = 0 = \Delta G^\circ + \mathrm{RTln}Q$ *(Q=K)*
  - $\Delta G^\circ = -\mathrm{RTln}K$



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Under std conditions Q=1 and lnQ=0, so $\Delta G = \Delta G^\circ + RT\ln Q$ then becomes $\Delta G = \Delta G^\circ$

Example - ΔG

Calculate ΔG at 427°C for the reaction

$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

if the P_{N2} = 33.0 atm, P_{H2}= 99.0 atm, and P_{NH3}= 2.0 atm

$$Q = \frac{P_{NH3}^{\ 2}}{P_{N2}^{\ 1} \times P_{H2}^{\ 3}} = \frac{(2.0\ atm)^2}{(33.0\ atm)^1\ (99.0)^3} = 1.2 \times 10^{-7}$$

Using: $\Delta H^o_{reaction} = \Sigma n H^o_f(products) - \Sigma n H^o_f(reactants)$

$\Delta H° = [\ 2(-46.19)] - [0 + 3(\ 0)] = -92.38\ kJ = -92380\ J$

$\Delta S^o_{reaction} = \Sigma n S^o_f(products) - \Sigma n S^o_f(reactants)$

$\Delta S° = [2\ (192.5)] - [(191.50) + 3(130.58)] = -198.2\ J/K$

Example - ΔG

Calculate ΔG at 427°C for the reaction

$$N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$$

if the P_{N2} = 33.0 atm, P_{H2}= 99.0 atm, and P_{NH3}= 2.0 atm

$$\Delta G^\circ_{reaction} = \Delta H^\circ_{reaction} - T\Delta S^\circ_{reaction}$$

$$\Delta G^\circ = -92380\ J - (700\ K)(-198.2\ J/K)$$

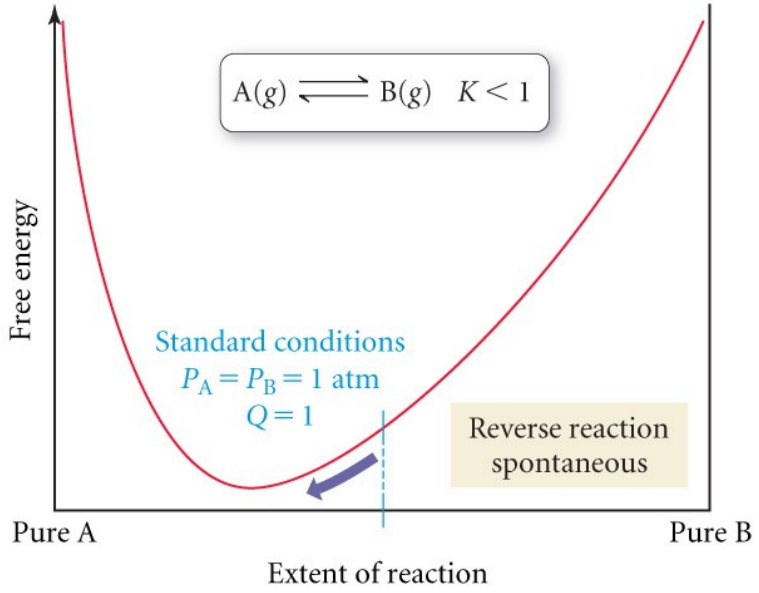
$$\Delta G^\circ = +46400\ J$$

$$\Delta G = \Delta G^\circ + RT\ln Q$$

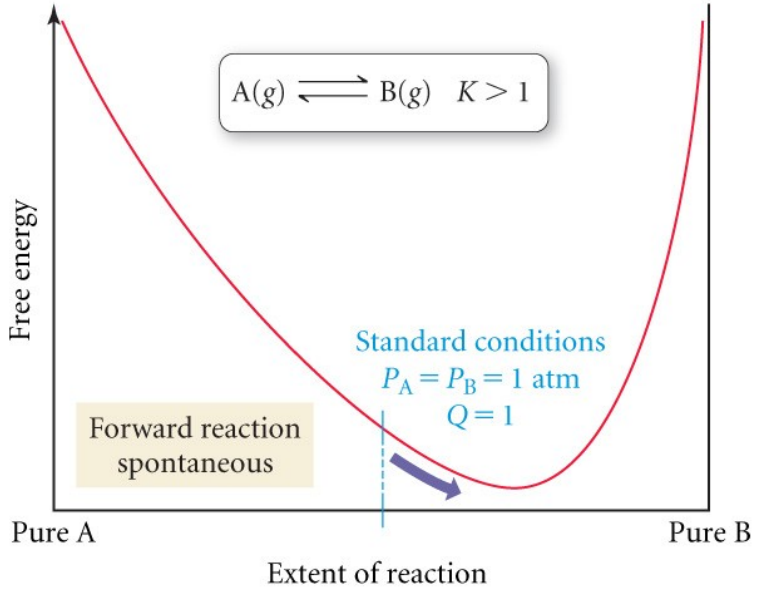
$$\Delta G = +46400\ J + (8.314\ J/K)(700\ K)(\ln 1.2 \times 10^{-7})$$

$$\Delta G = -46300\ J = -46\ kJ$$

Free Energy and the Equilibrium Constant



(a)



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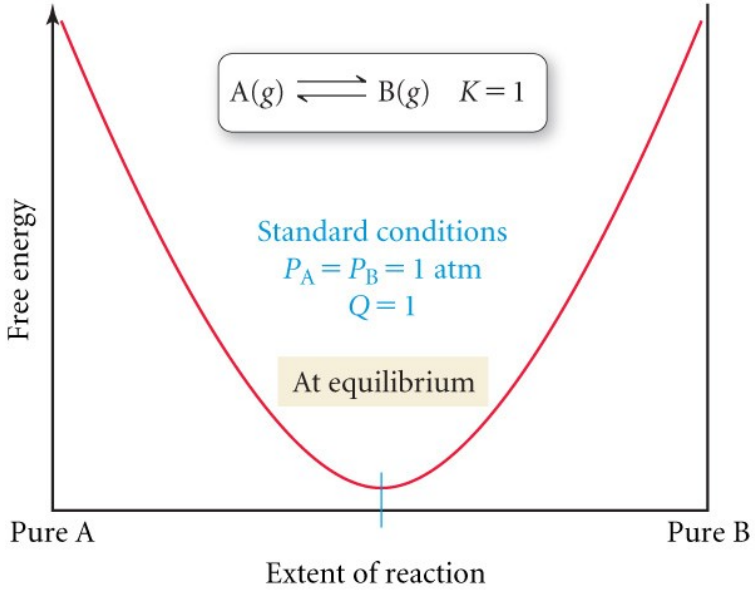

(c)

Example - K

- Estimate the equilibrium constant and position of equilibrium for the following reaction at 427°C

$$N_2(g) + 3\ H_2(g) \Leftrightarrow 2\ NH_3(g)$$

$$\Delta H° = [\ 2(-46.19)] - [0 + 3(\ 0)] = -92.38\ kJ = -92380\ J$$

$$\Delta S° = [2\ (192.5)] - [(191.50) + 3(130.58)] = -198.2\ J/K$$

$$\Delta G° = -92380\ J - (700\ K)(-198.2\ J/K)$$

$$\Delta G° = +46400\ J$$

Example - K

- Estimate the equilibrium constant and position of equilibrium for the following reaction at 427°C

$$N_2(g) + 3\ H_2(g) \Leftrightarrow 2\ NH_3(g)$$

$$\Delta G° = -RT\ \ln K$$

$$+46400\ J = -(8.314\ J/K)(700\ K)\ \ln K$$

$$\ln K = -7.97$$

$$K = e^{-7.97} = 3.45 \times 10^{-4}$$

e K is << 1, the position of equilibrium favors react

Temperature Dependence of K

$$\ln K = -\frac{\Delta H^\circ_{rxn}}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ_{rxn}}{R}$$

y = m x + b

Thermodynamics of Hell

The following is an actual question given on a University of Washington chemistry mid-term. The answer by one student was so "profound" that the professor shared it with colleagues, via the Internet, which is, of course, why we now have the pleasure of enjoying it as well.

Is Hell exothermic (gives off heat) or endothermic (absorbs heat)?

Most of the students wrote proofs of their beliefs using Boyle's Law, (gas cools off when it expands and heats up when it is compressed) or some variant.

One student, however, wrote the following:

First, we need to know how the mass of Hell is changing in time. So we need to know the rate that souls are moving into Hell and the rate they are leaving. I think that we can safely assume that once a soul gets to Hell, it will not leave. Therefore, no souls are leaving.

As for how many souls are entering Hell, let’s look at the different religions that exist in the world today. Some of these religions state that if you are not a member of their religion, you will go to Hell. Since there are more than one of these religions and since people do not belong to more than one religion, we can project that all souls go to Hell. With birth and death rates as they are; we can expect the number of souls in Hell to increase exponentially.

Now, we look at the rate of change of the volume in

This gives two possibilities:
1. If Hell is expanding at a slower rate than the rate at which souls enter Hell, then the temperature and pressure in Hell will increase until all Hell breaks loose.

2. If Hell is expanding at a rate faster than the increase of souls in Hell, then the temperature and pressure will drop until Hell freezes over.

So which is it?
If we accept the postulate given to me by Teresa during my Freshman year, "...that it will be a cold day in Hell before I sleep with you," and take into account the fact that I still have not succeeded in having sexual relations with her, then, #2 cannot be true, and thus I am sure that Hell is exothermic and will not freeze.